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FREE ENERGY OF A SOLID SOLUTION ON A  
FACE-CENTERED CUBIC LATTICE

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FREE ENERGY OF A SOLID SOLUTION ON A  
FACE-CENTERED CUBIC LATTICE

[This is a full translation of an article submitted by Ting Hou-ch'ang, Ch'iao Teng-chiang and Chang Tsung-sui, appearing in Wu-li Hsueh-pao (Acta Physica Sinica), Vol XIII, No 6, Peiping Nov 1957; pp 515-524.]

ABSTRACT

This paper applies Kirkwood's method for calculating the configurational free energy  $F$  of a solid solution to a solid solution  $AB_3$  inhabiting a face-centered cubic lattice. In this method, the free energy  $F$  is expressed as a series in  $(kT)^{-1}$ , and our calculation goes as far as the coefficient of  $(kT)^{-4}$ .

If the order of the solid solution is denoted by  $S$  and the free energy on neglecting  $O(kT)^{-n}$  by  $F_n$ , the relation between  $F_n$  and  $S$  are found to depend on  $n$  in a marked manner. In particular,  $F_3$  and  $F_5$  have always a minimum at  $S=0$ , implying no superlattice may exist. The foregoing is actually nothing but an indication of the slow convergence for the expansion of  $F$  in  $(kT)^{-1}$ .

On expressing  $F$  as a series in

$$\eta \equiv \exp \{ - (V_{AA} + V_{BB} - 2V_{AB})/kT \} - 1$$

where  $V_{AA}$ ,  $V_{BB}$  and  $V_{AB}$  are interaction energies between AA, BB and AB pairs of nearest neighbors and denoting by  $F'_n$  the free energy on neglecting  $O(\eta^n)$ , we find that  $F'_2$  and  $F'_3$  do not give us any super-

lattice, but  $F'_4$ ,  $F'_5$  do. In fact, from  $F'_4$ ,  $F'_5$ , we get a sudden change of  $S$  accompanied by a latent heat, just as in the earlier theories.  $F'_4$ ,  $F'_5$  behave similarly, so we may hope they approximate the actual free energy.

## I. INTRODUCTION

The purpose of this short article is to apply Kirkwood's<sup>(1)</sup> method for calculating the free energy of solid solution of a face-centered lattice and through which to discuss related questions of superlattice.

There were quite a few theories of superlattice of face-centered cubic lattice. In 1935, Bragg and Williams<sup>(2)</sup> offered a primary theory. Since Bethe<sup>(3)</sup> proposed a method for discussing the superlattice of AB type crystal, Peierls<sup>(4)</sup> had applied this method to study questions of face-centered cubic lattice. There was one point in his result that disagreed with fact. According to his theory, the superlattice of  $\text{AuCu}_3$  alloy under any low temperature does not correspond with stable equilibrium. Applying expanded chemical method must also take a group of proper lattice-point to calculate the number of various neighboring pairs and then the conclusion<sup>(5)</sup> of existence of superlattice can be drawn. Even then, there is still a great distance between the results of Bragg-William method and chemical method as far as the quantity is concerned, such as the sudden change in the dropping of critical temperature.

As to the application of Kirkwood method for solving questions of face-centered lattice, Nis and Shockley had discussed it in a thesis.

They calculated Thiele's semi-invariable  $\lambda_2$  [Also the coefficient of  $(kT)^{-2}$  in the series for the expansion of  $F$  in  $(kT)^{-1}$ ]. But it is not hard to notice that if neglecting  $O(kT)^{-3}$  in the series for the expansion of  $F$  in  $(kT)^{-1}$ , then the phenomenon of superlattice is nonexistence.

In this article we apply this method to calculate high power term<sup>1)</sup> of expansion of free energy, and calculate coefficients<sup>(7)</sup> of  $(kT)^{-3}$  and  $(kT)^{-4}$ . There are two reasons: Firstly, Kirkwood method is strict and it is worthwhile to applying it for calculating the free energy. Secondly, the structural feature of face-centered<sup>lattice</sup> is that neighbors of any lattice-point can be mutually neighboring to each other (This point<sup>does</sup> not appear in AB type lattice). The interaction between neighbors does not appear in  $\lambda_1$  and  $\lambda_2$  but appear in  $\lambda_3$ . Thus, for the apprehension of feature of face-centered lattice, we must calculate  $\lambda_3$ .

The result of calculation is this. When we neglect  $\lambda_4, \lambda_5, \dots$  etc (neglecting  $O((kT)^{-4})$ ), we could only notice the sudden change in the specific heat but not the latent heat in the theoretical result, just like the case of AB type. And when we neglect  $\lambda_5, \lambda_6, \dots$  etc (neglecting  $O((kT)^{-5})$ ), we could not notice any sudden change in theoretical result.

This does not mean that Kirkwood method is doubtful. It only indicates the slow convergence for the expansion of  $F$  in  $(kT)^{-1}$  at the neighborhood of our studying temperature  $T$ . Obviously, the distribution function of solid solution is the polynomial of (see 1) Professor Wang Chu-chi indicated that he worked on this in 1943 but the result was not published

following paragraph for above terms)

$$\exp[-(V_{AA}+V_{BB}-2V_{AB})/kT]$$

Then, it is also the polynomial of

$$\eta \equiv \exp\{-(V_{AA}+V_{BB}-2V_{AB})/kT\} - 1$$

Therefore, the expansion of free energy in  $\eta$  is possible. And this expansion seems more reasonable than the expansion of  $F$  in  $(kT)^{-1}$ . In this expansion, if we neglect  $O(\eta^2)$  or  $O(\eta^3)$ , we could not notice any sudden change. But if we neglect  $O(\eta^4)$  or  $O(\eta^5)$ , we could obtain latent heat. This result is obviously more reliable than the result from the discussion of expansion of  $F$  in  $(kT)^{-1}$ . (see paragraph III for details)

## II COURSE OF CALCULATION

The calculation here is identical to calculation in item [8] in the bibliography. We want to indicate here <sup>only</sup> the difference in calculation between ours and those of that paper.

A face-centered cubic lattice can be considered as a cross-locked structure of four simple cubic lattice. The points of lattice of these four simple cubic lattice can be represented by  $a$ ,  $b_1$ ,  $b_2$ , and  $b_3$ . When we let  $a$  point occupying the top of a typical cube,  $b$  and so forth will then occupy the centers of six faces of the cube. The three unit lattice  $b_1$ ,  $b_2$ , and  $b_3$  are identical as far as their positions in the crystal is concerned. In the following calculation we will use  $b$  to represent their points and not to separate  $b_1$ ,  $b_2$ , and  $b_3$ . This simplifies calculation.

Let A and B as two kinds of atoms of solid solution. Introducing

$\xi_a, \xi_b, \lambda_{ab}$ , and  $\lambda_{bb'}$ , the definitions are:

$$\begin{aligned}
 \xi_a &= 1 && \text{when } a \text{ has one A atom,} \\
 &= 0 && \text{when } a \text{ has one B atom;} \\
 \xi_b &= 1 && \text{when } b \text{ has one A atom,} \\
 &= 0 && \text{when } b \text{ has one B atom;} \\
 \lambda_{ab} &= 1 && \text{when } a \text{ and } b \text{ are nearest neighbors,} \\
 &= 0 && \text{when } a \text{ and } b \text{ are not nearest neighbors;} \\
 \lambda_{bb'} &= 1 && \text{when } b \text{ and } b' \text{ are nearest neighbors,} \\
 &= 0 && \text{when } b \text{ and } b' \text{ are not nearest neighbors;}
 \end{aligned} \tag{1}$$

where  $b$  and  $b'$  represent different  $b$  lattice-point. Let  $4N$  represents number of points of entire crystal,  $N\theta$  as the number of A atom in  $a$  unit.lattice, and  $3N\theta'$  as the number of A atom in  $b$  unit.lattice, we have

$$\sum_i \xi_a = N\theta, \quad \sum_i \xi_b = 3N\theta'. \tag{2}$$

Let  $V_{AA}, V_{BB}, V_{AB}$  express the interaction energies of neighboring AA, BB and AB pairs respectively, then the potential energy of the crystal obviously is 1)

$$\text{Constant} + V [\sum \lambda_{ab} \xi_a \xi_b + \frac{1}{2} \sum \lambda_{bb'} \xi_b \xi_{b'}]. \tag{3}$$

$$V = V_{AA} + V_{BB} - 2V_{AB}.$$

where the term in the bracket is neighboring number of AA pair which can be represented by  $X$ . Thus, the distribution function  $\Omega$  of solid solution of face-centered lattice can be written as [neglecting the constant in (3)]

1) (3) can be proved as follows: potential energy as

$$\begin{aligned}
 &\sum \lambda_{ab} [\xi_a \xi_b V_{AA} + (1-\xi_a)(1-\xi_b) V_{BB} + (1-\xi_a)\xi_b V_{AB} + \xi_a(1-\xi_b) V_{AB}] + \\
 &+ \sum \frac{1}{2} \lambda_{bb'} [\xi_b \xi_{b'} V_{AA} + (1-\xi_b)(1-\xi_{b'}) V_{BB} + (1-\xi_b)\xi_{b'} V_{AB} + \xi_b(1-\xi_{b'}) V_{AB}].
 \end{aligned}$$

By applying (2) and following (12) & (13), above equation can be reduced to expression (3)

$$\Omega(\theta, \theta', T) = \sum f(4N, N\theta, 3N\theta', X) e^{aX}, \quad (5)$$

where  $a$  represents  $-V/kT$ ;  $f(4N, N\theta, 3N\theta', X)$  represents distribution number for distribution of  $N\theta, 3N\theta'$  number of A atoms in a face-centered lattice solid solution of  $4N$  total points of lattice. In distribution,  $N\theta$  number of A atoms are placed on  $a$  unit cell,  $3N\theta'$  of A atoms are placed on  $b$  unit cell, and at the same time let the adjacent number of AA pair as  $X$ . According to methods in [1] and [8], the above equation can be change to

$$\Omega(\theta, \theta', T) = (\sum f) (1 + aM_1 + \frac{1}{2!} a^2 M_2 + \dots), \quad (6)$$

where  $M_n$  represents the average of  $X^n$  under various distribution. See item [8] in bibliography for meaning. Since

$$(\sum f) = \binom{V}{N\theta} \binom{3N}{3N\theta'}. \quad (7)$$

after  $M$  is obtained,  $\log \Omega$  can be expressed as

$$\log \binom{V}{N\theta} \binom{3N}{3N\theta'} + \sum_{i=1}^{\infty} \lambda_i (kT)^{-i},$$

therefore free energy can be expressed as

$$-kT \left\{ \log \binom{V}{N\theta} \binom{3N}{3N\theta'} + \sum \lambda_i (kT)^{-i} \right\}. \quad (8)$$

see [8] for relationship of  $\lambda$  and  $M$ .

Just as indicated in thesis [8], the main problem is to obtain  $M_n$ , the  $M_n$  here is

$$\left\langle \left( \sum \lambda_{i_1} \xi_{i_1} \xi_{i_1} + \frac{1}{2} \sum \lambda_{i_1 i_2} \xi_{i_1} \xi_{i_2} \right)^n \right\rangle.$$

where  $\langle \rangle$  represents average, with reference to [1] and [8]. For obtaining the above, the term in the bracket is expanded. Therefore the terms we wish to obtain are terms of

$$\sum \lambda_{i_1} \lambda_{i_2} \lambda_{i_3} \dots \langle \xi_{i_1} \xi_{i_2} \dots \rangle \langle \xi_{i_3} \xi_{i_4} \dots \rangle \quad (9)$$

and the like. In these kind of expressions,  $d, d', \dots$  are not equal, and  $b, b', \dots$  are also not equal to each other. And any lower mark  $a, a', \dots, b, b', \dots$  can appear more than once (see [8]).

Since  $\langle \xi_a \xi_{a'} \rangle, \langle \xi_b \xi_{b'} \rangle$  and the positions of  $a, a', \dots, b, b', \dots$  have no relationship, (9) becomes  $\langle \xi_a \xi_{a'} \rangle, \langle \xi_b \xi_{b'} \rangle$  times

$$\sum \lambda_{ab} \lambda_{a'b'} \dots \quad (10)$$

utilize method used in [8], we can obtain

$$\left. \begin{aligned} \langle \xi_a \rangle &= \theta, \\ \langle \xi_a \xi_{a'} \rangle &= N\theta(N\theta - 1)/N(N - 1), \dots, \\ \langle \xi_b \rangle &= \theta', \\ \langle \xi_b \xi_{b'} \rangle &= 3N\theta'(3N\theta' - 1)/3N(3N - 1), \dots \end{aligned} \right\} \quad (11)$$

as to the calculation of expression similar to expression (10), we start from

$$\sum_i \lambda_{ai} = z, \quad \sum_a \lambda_{ai} = \frac{1}{3} z, \quad \sum_{i,j} \lambda_{ij} = \frac{2}{3} z \quad (12)$$

(where  $z$  represents total neighboring number of a lattice point which equals 12). We can obtain

$$\left. \begin{aligned} \sum_{a,b} \lambda_{ab} &= Nz, \\ \sum_{b,b'} \lambda_{bb'} &= 2Nz, \\ \sum_{a,b} \lambda_{ab} \lambda_{a'b'} &= Nz \left( \frac{1}{3} z - 1 \right), \\ \sum_{a,b} \lambda_{ab} \lambda_{ab'} &= Nz(z - 1), \dots \end{aligned} \right\} \quad (13)$$

and so forth. The method used is the same as the method in thesis [8].

Therefore we are not going to show the details. We put various kind of expression (10) containing two or three  $\lambda$  in the appendix as reference material for our readers.

The results are:



$$\lambda_1 = Nz(\theta\theta' + \theta'^2),$$

$$\lambda_2 = Nz\theta\theta'(1-\theta)(1-\theta') + Nz\theta'^2(1-\theta')^2,$$

$$\lambda_3 = Nz\theta\theta'(1-\theta)(1-\theta')(1-2\theta)(1-2\theta') + Nz\theta'^2(1-\theta')^2(1-2\theta')^2 +$$

$$+ NY\theta'^2(1-\theta')^2\{3\theta(1-\theta) + \theta'(1-\theta')\},$$

$$\lambda_4 = Nz\theta\theta'(1-\theta)(1-\theta')(1-6\theta+6\theta^2)(1-6\theta'+6\theta'^2) +$$

$$+ Nz\theta'^2(1-\theta')^2(1-6\theta'+6\theta'^2)^2 + 6N(Y_1-2z)\theta^2\theta'^2(1-\theta)^2(1-\theta')^2 +$$

$$+ 3N(Y_2-2z)\theta'^4(1-\theta')^4 + 12NY_3\theta\theta'^3(1-\theta)(1-\theta')^2 +$$

$$+ 6NY\theta'^2(1-\theta')^2(1-2\theta')\{\theta'(1-\theta')(1-2\theta') +$$

$$+ 2\theta(1-\theta)(1-2\theta) + \theta(1-\theta)(1-2\theta')\}.$$
(14)

where Y represents common value of

$$N^{-1}\sum \lambda_{ab}\lambda_{ab'}\lambda_{bb'}, \quad (15.1)$$

$$N^{-1}\sum \lambda_{bb'}\lambda_{bb''}\lambda_{b'b''}, \quad (15.2)$$

$Y_1, Y_2, Y_3$  represent separately

$$\left. \begin{aligned} N^{-1}\sum \lambda_{ab}\lambda_{ab'}\lambda_{a'b'b'}, \\ N^{-1}\sum \lambda_{bb'}\lambda_{bb''}\lambda_{b'b''}\lambda_{b'b''}, \\ N^{-1}\sum \lambda_{ab}\lambda_{bb'}\lambda_{b'b''}\lambda_{a'b''}. \end{aligned} \right\} \quad (16)$$

to prove (15.1) equal to (15.2), let  $\hat{Z}_{ab}$  as common neighboring number of a pair of nearest neighbors  $a$  and  $b$ . Obviously, it equals to 4, thus

$$\sum \lambda_{ab}\lambda_{ab'}\lambda_{bb'} = \sum_{ab} \lambda_{ab}\hat{Z}_{ab} = \sum_{ab} \lambda_{ab}4 = 4Nz. \quad (17)$$

meanwhile, let  $\hat{Z}_{bb'}$  as the common neighboring number of a pair of nearest neighbors  $b$  and  $b'$ , which is also 4, thus

$$\begin{aligned}\sum \lambda_{bb'} \lambda_{b'b} \lambda_{bb} &= \sum \lambda_{bb'} (\lambda_{b'b} \lambda_{bb} + \lambda_{b'a} \lambda_{ba}) - \sum \lambda_{bb'} \lambda_{b'a} \lambda_{ba} = \\ &= \sum \lambda_{bb'}^2 \lambda_{bb} - \sum \lambda_{ab} \lambda_{ab'} \lambda_{bb'} = 2Nz \cdot 4 - 4Nz = 4Nz.\end{aligned}\quad (18)$$

this concurrently proves  $Y = 48$ . As to the  $Y_1$ ,  $Y_2$ , and  $Y_3$ , we have the following equations:

$$\left. \begin{aligned}Y_1 &= N^{-1} \left\{ \sum_{bb'} \left[ \sum_a \lambda_{ab} \lambda_{ab'} \right]^2 - \sum \lambda_{ab} \lambda_{ab'} \right\}, \\ Y_2 &= N^{-1} \left\{ \sum_{bb'} \left[ \sum_{b''} \lambda_{bb'} \lambda_{b'b''} \right]^2 - \sum \lambda_{bb'} \lambda_{b'b''} \right\}, \\ Y_3 &= N^{-1} \left\{ \sum_{ab} \left[ \sum_{b'} \lambda_{ab} \lambda_{bb'} \right]^2 - \sum \lambda_{ab} \lambda_{bb'} \right\};\end{aligned}\right\} \quad (19)$$

and we obtain

$$Y_1 = 72, \quad Y_2 = 144, \quad Y_3 = 144 \quad (20)$$

For the sake of proving equation (14) we may discuss the specific condition of  $\theta = \theta'$ , at which

$$X = \frac{1}{2} \sum \lambda_{cc'} \xi_{cc'} \xi_{cc'} \quad (21)$$

where  $C$  represents any point on the crystal lattice. The calculation is totally the same as the calculation of free energy of AB type crystal. The only difference is the values of

$$\sum \lambda_{cc'} \lambda_{cc'} \dots \quad (22)$$

and so forth. To the AB type,

$$\sum \lambda_{cc'} \lambda_{c'c} \lambda_{cc} = 0, \quad (23)$$

$$\sum \lambda_{cc'} \lambda_{c'c} \lambda_{cc'} \lambda_{c'c} = \sum \lambda_{ab} \lambda_{ba} \lambda_{ab'} \lambda_{b'a} + \sum \lambda_{ba} \lambda_{ab} \lambda_{ba'} \lambda_{ab'}, \quad (24)$$

To the AB type lattice, if we also let  $4N$  as the total number of lattice point, then the definition of  $y$  in thesis [8] should be

$$(2N)^{-1} \sum \lambda_{ab} \lambda_{ab} \lambda_{ab} \lambda_{ab},$$

thus, the right <sup>hand</sup> side of (24) becomes  $4Ny$ . Therefore, if we let  $Y$  in equation (14) as 0 and  $2Y_1 + 4Y_3 + Y_2$  as  $4y$ , equation (14) should be

AB type's corresponding result which is the same as the corresponding result in thesis [8]. Of course, for the sake of comparison, we must multiply 4 to the result in [8] because the total <sup>number of</sup> lattice point here is 4N and the total number of lattice point in [8] is N. Based on this point and from the result in [8] we could almost guess the possessive term in equation (14) outside of Y. The term containing Y is our most important term.

### III DISCUSSION ON THE RESULT

Introduce the presumption of  $\theta + 3\theta' = 1$  which also mean that let N as the total number of A atom and introduce the values of Z, Y, ... and so forth, we obtain

$$\begin{aligned} & \frac{1}{NkT} \left[ F(\theta) - F\left(\frac{1}{4}\right) \right] \\ &= \theta \ln \theta + (1-\theta) \ln(1-\theta) + (1-\theta) \ln \frac{(1-\theta)}{3} + (2+\theta) \ln \frac{2+\theta}{3} + 4 \ln 4 - 3 \ln 3 + \\ &+ \left\{ 1.5 - \frac{4}{3} (1+\theta - 2\theta^2) \right\} \alpha + \left\{ 0.422 - \frac{1}{27} (2+7\theta - 15\theta^2 + \theta^3 + 5\theta^4) \right\} \alpha^2 + \\ &+ \left\{ 0.246 - \frac{4}{81} (2+25\theta - 54\theta^2 - 5\theta^3 + 50\theta^4 - 6\theta^5 - 12\theta^6) \right\} \alpha^3 + \\ &+ \left\{ 0.206 - \frac{1}{4874} (236 + 509\theta - 6958\theta^2 - 19174\theta^3 + 32894\theta^4 + \right. \\ &\quad \left. + 1964\theta^5 - 19672\theta^6 + 1976\theta^7 + 3644\theta^8) \right\} \alpha^4 + \dots \end{aligned} \quad (25)$$

where F represents free energy. Under different temperature, the dependence of  $[F(\theta) - F(\frac{1}{4})]/kT$  to  $\theta$  can be illustrated by figure. In the above equation when only  $\alpha$  term is retained, the curve tells us that we have a sudden change of one  $\theta$  and latent heat shown in the sudden change. When only  $\alpha, \alpha^2$  terms are retained, the curve tells us

we do not have sudden change. The condition is the same when  $a, a^2, a^3, a^4$  are retained. The curve shown by retaining  $a, a^2, a^3$  tells us that our  $\frac{d\theta}{dT}$  has a sudden change which corresponds to the condition where critical heat has sudden change. We do not intend to plot these curves here.

From this we can see that the above showing is because at the neighborhood of our concerned temperature, the convergence of equation (25) is very slow. Therefore when retaining  $a, a^2$  and also when retaining  $a, a^2, a^3, a^4$ , the most important term in the free energy expression becomes the term at the end. And the symbol of end term has no relation with the symbol of  $V_{AA} + V_{BB} - 2V_{AB}$ . Because the forming of superlattice is mainly due to  $V_{AA} + V_{BB} - 2V_{AB} > 0$ .  $a^2, a^4$  terms have no relationship with the formation of superlattice. This also means that when retaining  $a, a^2$ , and ~~when~~ also when retaining  $a, a^2, a^3, a^4$ , the most important term in the free energy expression has no relation with the forming of superlattice. This is why the  $F - \theta$  curve has the above showing.

To avoid the above mentioned faults, the expansion of  $F$  in  $(kT)^{-1}$  can be changed to ~~Exp~~ expansion of  $F$  in

$$\eta = \exp\{-(V_{AA} + V_{BB} - 2V_{AB})/kT\} - 1 = \exp \alpha - 1 \quad (26)$$

According to the definition of distribution function, it is polynomial of  $\exp \alpha$ . It is also the polynomial of  $\eta$ . Therefore, when free energy is expressed as

$$-kT \left\{ \log \left( \frac{N}{N\theta} \right) \left( \frac{3N}{3N\theta'} \right) + g(\theta, \theta', T) \right\}$$

$g$  should be expressed as a series of  $\eta$ . This atleast is more reasonable as it is expressed as a series of  $(kT)^{-1}$ . Thus, we obtain

$$\begin{aligned}
 \left[ F(\theta) - F\left(\frac{1}{3}\right) \right] / NkT = & \theta \ln \theta + (1-\theta) \ln(1-\theta) + (1-\theta) \ln \frac{(1-\theta)}{3} + \\
 & + (2+\theta) \ln \frac{2+\theta}{3} + 4 \ln 4 - 3 \ln 3 + \left[ 1.5 - \frac{4}{3} (1+\theta-2\theta^2) \right] \eta + \\
 & + \left[ -0.3280 - \frac{4}{27} (-2.5 + 2.5\theta - 6\theta^2 + \theta^3 + 5\theta^4) \right] \eta^2 + \\
 & + \left[ 0.3241 - \frac{4}{81} (5 + 13\theta - 27\theta^2 - 8\theta^3 + 35\theta^4 - 6\theta^5 - 12\theta^6) \right] \eta^3 + \\
 & + \left[ -0.1513 + \frac{1}{2 \times 3^7} (682 + 310\theta - 4544\theta^2 + 16960\theta^3 - 19664\theta^4 - 3908\theta^5 + \right. \\
 & \left. + 15784\theta^6 - 1976\theta^7 - 3644\theta^8) \right] \eta^4 + \dots
 \end{aligned} \tag{27}$$

due to the presumption of  $V_{AA} + V_{BB} - 2V_{AB} > 0$ , the change of  $\eta$  is within  $(0, -1)$ . Therefore the convergence of the above expansion is comparatively good. When we only retain  $\eta$  and neglect  $O(\eta^2)$ ,  $F-\theta$  curve tells us that we do have any sudden change. The right <sup>hand</sup> side of (27) at this instance has the same pattern as the right <sup>hand</sup> side of (25) retaining  $(kT)^{-1}$  term only. But zone of change of  $\eta$  here is from  $-1$  to zero and the change of  $a$  in (25) is from  $(-\infty)$  to zero. Therefore even <sup>when</sup> the patterns are the same, "no sudden change" is still possible. When we retain  $\eta$ ,  $\eta^2$ , but neglect  $O(\eta^3)$  in the right side of (27),  $\theta$  still has no sudden change. When we retain  $\eta$ ,  $\eta^2$ ,  $\eta^3$  but neglect  $O(\eta^4)$  in (27), we notice the sudden change of  $\theta$ . The critical case is as follows:

$$\eta = -0.984, \quad \frac{V}{kT} = 4.13, \quad \theta_c = 0.85. \tag{28}$$

when we retain  $\eta$ ,  $\eta^2$ ,  $\eta^3$ ,  $\eta^4$  but neglect  $O(\eta^5)$  in (27), we still have the sudden change in  $\theta$ .

$$\eta_c = -0.954, \quad \frac{V}{kT_c} = 3.08, \quad \theta_c = 0.90. \quad (29)$$

the  $F-\theta$  curves of these two cases are nearly identical. Therefore, we believe that they are quite near the real  $F-\theta$  curve which also means that it is not neglecting right <sup>hand</sup> side (27) of any  $\eta$  exponent.

For comparison, we list the result ~~is~~ advanced by Yang Chen-ning <sup>5</sup>:

$$\frac{V}{kT_c} = 2.432, \quad \theta_c = 0.9556. \quad (30)$$

for reference, we also show the  $F-\theta$  curve obtained from retaining of  $\eta, \eta^2, \eta^3, \eta^4$ , in (27).

Here we shell point out that prior to the introduction of  $\eta^3$  term, the sudden change will not appear. And  $\eta^3$  term basically is influenced by the action of three adjacent atoms contained therein. In other word, in our theoretical equation (27), when we consider the sudden change, we must consider the interaction <sup>between</sup> neighbors. In earlier theories this point was not significant.

(Cont'd on following page)

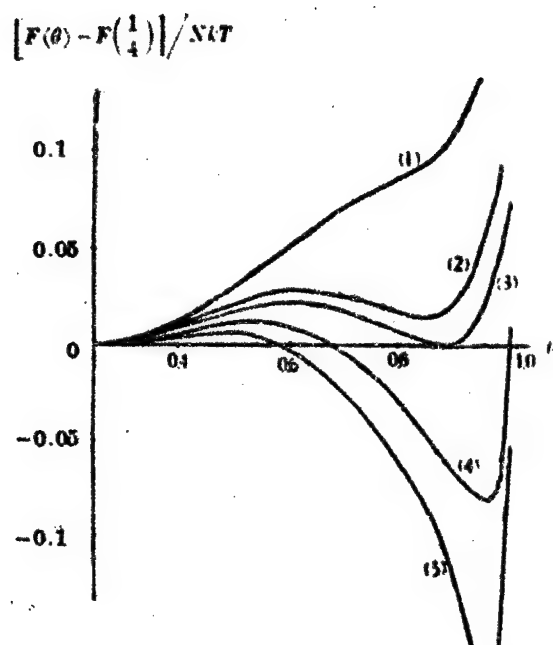


Fig. 1

The relationship of  $\left\{ F(\theta) - F\left(\frac{1}{4}\right) \right\} / NkT$  and  $\theta$

- (1)  $\eta = -0.9$     (2)  $\eta = -0.94$     (3)  $\eta = \eta_c = -0.954$   
 (4)  $\eta = -0.98$     (5)  $\eta = -1$

#### APPENDIX

We list here equations similar to (10) with respective values of containing two and three  $\eta$  for reference.

$$\sum \lambda_{ab} \lambda_{a'b} = Nz \left( \frac{1}{3} z - 1 \right),$$

$$\sum \lambda_{ab} \lambda_{ab'} = Nz(z-1),$$

$$\sum \lambda_{ab} \lambda_{a'b'} = Nz \left( Nz - \frac{4}{3} z + 1 \right),$$

$$\sum \lambda_{ab} \lambda_{bb'} = \frac{2}{3} Nz^2,$$

$$\sum \lambda_{ab} \lambda_{b'b'} = 2N^2 z^2 - \frac{4}{3} Nz^2,$$

$$\sum \lambda_{bb'} \lambda_{b'b'} = 2Nz \left( \frac{2}{3} z - 1 \right),$$

$$\sum \lambda_{bb'} \lambda_{b'b''} = 4N^2 z^2 - \frac{16}{3} Nz^2 + 4Nz,$$

$$\sum \lambda_{ab} \lambda_{ab'} \lambda_{ab''} = Nz(z-1)(z-2),$$

$$\sum \lambda_{ab} \lambda_{a'b} \lambda_{a'b'} = Nz(z-1) \left( Nz - \frac{5}{3} z + 2 \right),$$

$$\sum \lambda_{ab} \lambda_{ab'} \lambda_{ab''} = Nz(z-1) \left( \frac{1}{3} z - 1 \right),$$

$$\sum \lambda_{ab} \lambda_{a'b} \lambda_{a'b'} = N^3 z^3 + N^2 z^2 (3-4z) + \frac{2}{9} Nz^2 + 4(z-1)^2 Nz,$$

$$\sum \lambda_{ab} \lambda_{a'b} \lambda_{a'b''} = Nz \left( \frac{1}{3} z - 1 \right) \left( \frac{1}{3} z - 2 \right),$$

$$\sum \lambda_{ab} \lambda_{a'b} \lambda_{a'b'} = Nz \left( \frac{1}{3} z - 1 \right) \left( Nz - \frac{7}{3} z + 2 \right),$$

$$\sum \lambda_{ab} \lambda_{ab'} \lambda_{bb'} = NY,$$

$$\sum \lambda_{ab} \lambda_{ab'} \lambda_{bb''} = Nz(z-1) \cdot \frac{2}{3} z - NY,$$

$$\sum \lambda_{ab} \lambda_{ab'} \lambda_{bb''} = \frac{2}{3} Nz^2 (z-1) (3N-4) + 2NY,$$

$$\sum \lambda_{ab} \lambda_{a'b} \lambda_{bb'} = \frac{2}{3} Nz^2 \left( \frac{1}{3} z - 1 \right),$$

$$\sum \lambda_{ab} \lambda_{a'b} \lambda_{bb''} = \frac{2}{3} Nz^2 \left( \frac{1}{3} z - 1 \right) (3N-2),$$



$$\begin{aligned}
\sum \lambda_{ca} \lambda_{ab} \lambda_{bb} &= \frac{2}{9} Nz^3 - NY, \\
\sum \lambda_{ab} \lambda_{ca} \lambda_{bb} &= \frac{2}{3} Nz^2 \left( Nz - \frac{4}{3} z + 1 \right) - \frac{2}{9} Nz^3 + NY, \\
\sum \lambda_{ab} \lambda_{ca} \lambda_{bb} &= \frac{2}{3} Nz^2 \left( Nz - \frac{4}{3} z + 1 \right) (3N - 4) + \frac{4}{9} Nz^3 - 2NY, \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= \frac{2}{3} Nz^2 \left( \frac{2}{3} z - 1 \right), \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= 2Nz^2 \left( \frac{2}{3} z - 1 \right) (N - 1), \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= \frac{2}{3} Nz^2 \left( \frac{2}{3} z - 1 \right), \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= \frac{4}{3} Nz^2 \left( Nz - \frac{4}{3} z + 1 \right), \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= 4Nz^2 \left( N - \frac{4}{3} \right) \left( Nz - \frac{4}{3} z + 1 \right), \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= 2Nz \left( \frac{2}{3} z - 1 \right) \left( \frac{2}{3} z - 2 \right), \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= NY, \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= 2Nz \left( \frac{2}{3} z - 1 \right)^2 - NY, \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= 4Nz \left( \frac{2}{3} z - 1 \right) (Nz - 2z + 2) + 2NY, \\
\sum \lambda_{ab} \lambda_{bb} \lambda_{ba} &= \left( 4N^2 z^2 - \frac{16}{3} Nz^2 + 4Nz \right) \frac{2}{3} z (3N - 4) - \\
&\quad - 16Nz \left( \frac{2}{3} z - 1 \right) (Nz - 2z + 2) - 8NY.
\end{aligned}$$

Because it is too long, we do not list here <sup>expression</sup> (10) containing  
4  $\lambda$ .

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